

Translated from French by  
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(19) European Patent Office

(11) Publication No.: 0 509 922 A2

(12) EUROPEAN PATENT APPLICATION

(21) Application Number: 92401061.4

(22) Date of Filing: April 15, 1992

(51) Int. Cl.<sup>5</sup>: A61K 7/06

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(30) Priority: April 19, 1991 FR 9104886

(43) Date of Publication of the Application: Oct. 21, 1992 Bulletin 92/43

(84) Designated Contracting States:  
AT BE CH DE DK ES FR GB GR IT LI NL PT SE

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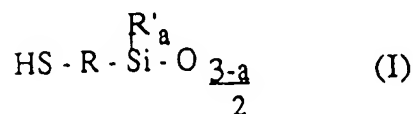
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(54) Composition and Process for Using Thiol Silicones for Protecting the Color of Dyed Keratin Fibers.

(57) The present invention pertains to the use of a polydiorganosiloxane containing a thiol functional group, which contains in its molecule at least one unit according to the formula

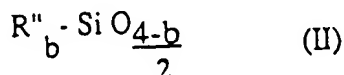


in which:

R denotes a divalent aliphatic radical containing 3 to 26 carbon atoms, which is possibly interrupted by an ester functional group and may carry ethylene oxide or propylene oxide or their mixtures as repeat units,

R' denotes a monovalent hydrocarbon radical containing 1 to 6 carbon atoms, an alkoxy radical containing 1 to 4 carbon atoms or trimethylsilyloxy;

a denotes an integer equaling 0, 1 or 2, the remaining units having the formula:



in which:

R'' denotes a C<sub>1</sub>-C<sub>18</sub> alkyl, C<sub>1</sub>-C<sub>6</sub> phenylalkyl or phenyl group;

b denotes an integer equaling 1, 2 or 3;

at least 50% of the groups R' and R'' denoting a methyl radical, as an agent for protecting the color of dyed keratin fibers.

The present invention pertains to the use of silicones containing thiol groups as agents for protecting the color of dyed hair, to compositions and processes involving the use of these silicones containing thiol groups.

It has been known for a long time that the artificial color of dyed hair tends to be attacked especially by light and shampooing agents, the color becoming more or more faint or becoming aesthetically rather unattractive or undesirable.

It therefore appeared to be necessary to protect the color of the dyed fibers and more particularly the dyed hair from external agents likely to fade the color or to change the initial color obtained after dyeing.

The inventor discovered, and this is the object of the present invention, that silicones containing thiol groups preserve the artificial color of dyed keratin fibers and especially of hair from degradations caused especially by light and shampooing. This property was demonstrated, in particular, by exposure to the artificial light of a solar simulator of the type of XENOTEST 150 from ORIGINAL HANAU or by washing under standard conditions by means of an AHIBA TEXOMAT G6B machine.

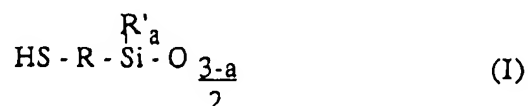
Consequently, the present invention pertains to the use of thiol silicones as agents for the protection of the color of dyed keratin fibers, particularly dyed hair.

Another object of the present invention is the compositions in which these thiol silicones are used.

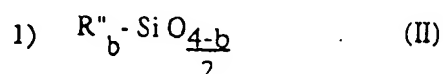
The present invention also pertains to a process for protecting the artificial color of keratin fibers, especially hair, against external agents, which process involves the use of the thiol silicones.

Other objects of the present invention appear from the reading of the specification and the following examples.

The thiol silicones used according to the present invention are polydiorganosiloxanes containing in their molecule at least one unit according to the formula:

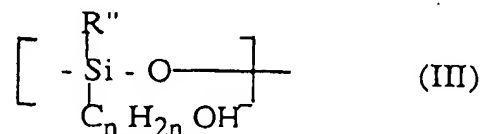


in which R denotes a divalent aliphatic radical containing 3 to 26 carbon atoms, which is possibly interrupted by an ester functional group and may carry ethylene oxide or propylene oxide or their mixture as repeat units, R' denotes a monovalent hydrocarbon radical containing 1 to 6 carbon atoms, an alkoxy containing 1 to 4 carbon atoms or trimethylsilyloxy;  $\underline{a}$  denotes an integer equaling 0, 1 or 2, the other units having the formula:



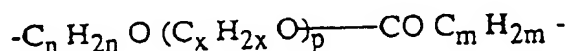
in which

R" denotes a C<sub>1</sub>-C<sub>18</sub> alkyl, (C<sub>1</sub>-C<sub>6</sub>) phenylalkyl or phenyl group;  
 b is an integer equaling 1, 2 or 3;  
 at least 50% of the groups R' and R" denoting a methyl group, and  
 2) possibly units according to the formula:



The amount of the thiol groups present in the polydiorganosiloxane used according to the present invention on a weight basis is between 0.1% and 15% and preferably between 0.15% and 13%.

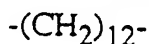
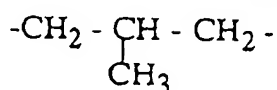
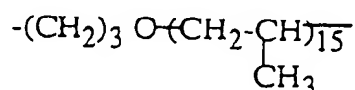
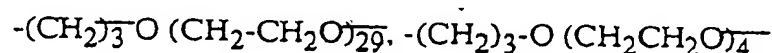
The radical R may denote, in particular, an alkylene group containing 3 to 8 carbon atoms, such as, more particularly, a (CH<sub>2</sub>)<sub>n</sub> group, in which n is between 3 and 8, or a group according to the formula:



in which n denotes an integer between 1 and 18, m denotes an integer between 1 and 8, x = 2 or 3, and if x = 3, the radical C<sub>3</sub>H<sub>6</sub> is branched[,]  
p equals 0 or denotes a number of up to 40.

R' denotes, more particularly, a C<sub>1</sub>-C<sub>6</sub> alkyl radical, such as methyl, ethyl, *n*-propyl, isopropyl or *n*-butyl.

The radical R" preferably denotes a methyl group, C<sub>12</sub>H<sub>25</sub> or 2-phenylpropyl;  
 the radical R denotes -(CH<sub>2</sub>)<sub>3</sub>,



and the radical R' denotes methyl or trimethylsilyloxy.

The total number of units (I), (II) and possibly (III) is preferably equal to or less than 500 and is, in particular, between 10 and 500.

The applicant observed that the polydiorganosiloxanes containing a thiol functional group as defined above were particularly effective in preserving the color of dyed hair from the deleterious effect of light and shampooing.

5           The polydiorganosiloxanes containing a thiol functional group are preferably used in amounts of at least 0.1% and generally in amounts between 0.1% and 20% and preferably in amounts between 1% and 10% in a composition containing a cosmetically acceptable medium suitable for being applied to keratin fibers, especially human hair.

10           Such compositions intended for application to dyed keratin fibers and particularly to dyed hair to protect the artificial color are in the form of oily or alcohol-based lotions, emulsions, aqueous or water-alcohol dispersions.

15           If the compositions intended for application to dyed keratin fibers and especially to hair are oily lotions, they contain, besides the polydiorganosiloxane with a thiol functional group, mineral, vegetable, animal or synthetic oils and more particularly isoparaffins, such as the ISOPARS or silicone oils, such as silicone oils with linear or cyclic structure, such as the polyalkylsiloxanes, the polyarylsiloxanes, the polyalkylarylsiloxanes, or the polyorganosiloxanes modified with organic functional groups different from the thiol groups as defined above or  
20           their mixture(s).

          The oily lotions may also contain waxes, resins or silicone gums together with the above-mentioned oils.

25           The alcohol-based lotions contain, besides the polydiorganosiloxane containing a thiol functional group, a lower alcohol containing 2 to 4 carbon atoms and preferably ethanol or isopropyl alcohol and possibly other organic solvents, such as the alkylene glycols or the glycol ethers.

30           If the compositions for dyed keratin fibers according to the present invention are in the form of emulsions, they form non-ionic or cationic and preferably non-ionic emulsions.

          The fatty phase of the emulsions is formed either exclusively by the polydiorganosiloxane containing a thiol functional group as defined above, or by a mixture of  
35           this polydiorganosiloxane with other oils or waxes as mentioned above for them oily lotions.

          The other phase of the emulsions is formed by an aqueous medium.

40           The non-ionic emulsions contain a non-ionic emulsifying agent selected from among the polyethoxylated fatty alcohols, the polyethoxylated fatty acids, the optionally polyethoxylated esters of sorbitan, the polyethoxylated or polyglycerolated alkyl phenols, the polyethoxylated or polyglycerolated fatty amides, the polyglycerolated fatty alcohols and alpha-diols; the number of polyethoxylated groups being between 2 and 50, the number of polyglycerol groups being between 2 and 30; the polyethoxylated fatty amides preferably containing 2 to 30 moles of  
45           ethylene oxide; the polyglycerolated fatty amides preferably containing 1 to 5 and especially 1.5 to 4 glycerol groups; the fatty acid esters of sorbitan preferably containing 2 to 30 moles of ethylene oxide.

5 The cationic emulsions contain a cationic emulsifying agent selected from among quaternary ammonium halides, such as dialkyl (C<sub>10</sub>-C<sub>30</sub>)-dimethyl ammonium, alkyl (C<sub>10</sub>-C<sub>30</sub>)-trimethyl ammonium or alkyl (C<sub>10</sub>-C<sub>30</sub>)-benzyl dimethyl ammonium and the polyethoxylated quaternary ammonium salts containing 2 to 30 moles of ethylene oxide. Distearyl dimethyl ammonium and behenyl trimethyl ammonium chloride are preferably used.

10 If the compositions used according to the present invention, which are intended for application to dyed keratin fibers and contain a thiol functional group, are dispersions, they contain, in addition to this agent, water and a dispersing agent or a suspending agent for the silicone in the aqueous medium. The more particularly preferred dispersing agents are selected from among a copolymer of ammonium acrylate and crosslinked polyacrylamide, a polyacrylamide, and a crosslinked acrylic acid polymer.

15 These dispersions may form non-rinsed or rinsed products as well as shampoos. In the latter case, they contain anionic, non-ionic, amphoteric surfactants or their mixtures at concentrations generally between 5 wt. % and 30 wt. %.

20 If the compositions according to the present invention contain solvents, these are selected more particularly from among the lower alkanols, such as ethanol.

25 The compositions according to the present invention may also contain any other agent usually applied to keratin fibers; if the compositions are applied to hair, these adjuvants are cosmetically acceptable adjuvants. These adjuvants may be selected, in particular, from among the colorants, preservatives, cosmetic resins, softening agents, perfumes, etc.

The compositions according to the present invention may also be in the form of sprays or they may be pressurized in aerosol-dispensing devices.

30 The process of protecting the artificial color of dyed keratin fibers and, in particular, dyed hair according to the present invention consists of applying to same a composition containing at least 0.1 % of a polydiorganosiloxane containing a thiol functional group containing units according to formulas (I) and (II) as defined above.

35 The keratin fibers and, in particular, the hair may be dyed by using colorants conventionally used for dyeing hair, e.g., by using oxidation dye precursors according to a dyeing process using an oxidizing agent or by so-called direct dyeing using benzonitro dyes, anthraquinone dyes, and azo dyes conventionally used for dyeing keratin fibers.

40 The use of thiol silicones according to the present invention is particularly suitable for hair dyed according to a dyeing process involving the use of an oxidizing agent.

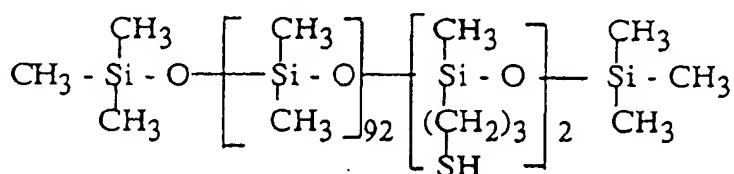
Compositions well known to the technician are described, e.g., in HARRY'S COSMETOLOGY, 7th edition, 1982, pp. 533-545.

45 The following examples are intended to illustrate the present invention without limiting its scope.

**EXAMPLE 1**

The following composition is prepared:

- Mixture of a polydimethylsiloxane carrying a hydroxyl group at the end of the chain and a cyclic polydimethylsiloxane, available under the name Q2-1401 from DOW-CORNING 65 g
- Polydimethylsiloxane available under the name SILBIONE HUILE 700 45V5, available from Rhône-Poulenc 15 g
- Polydimethylsiloxane, available under the name SILBIONE HUILE 700 45V2 from Rhône-Poulenc 15 g
- Polydiorganosiloxane with a thiol functional group according to the formula:



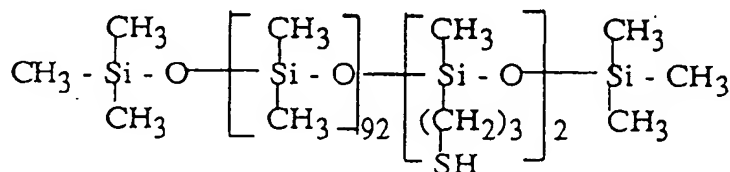
available under the name X2 8360 from DOW CORNING 5 g

This composition is in the form of an oil.

**EXAMPLE 2**

The following composition is prepared:

- Polydiorganosiloxane with a thiol functional group according to the formula:



- available under the name X2 8360 from DOW CORNING 5 g
- Cetyl alcohol ethoxylated with 2 moles of ethylene oxide 0.6 g
- Cetyl alcohol ethoxylated with 10 moles of ethylene oxide 0.4 g
- Water q.s.p. 100 g
- Spontaneous pH = 8.2

### EXAMPLE 3

- Sodium lauryl ether sulfate (C<sub>12</sub>-C<sub>14</sub> 70:30) with 2.2 moles of ethylene oxide in an aqueous solution with an active ingredient (AI) content of 28%, available under the name EMPICOL ESB/3FL from MARCHON

15 g AI

- Cocoyl betaine in an aqueous solution, 32%

2.4 g

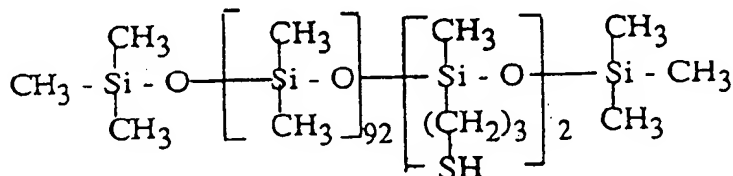
- Cetyl and hydroxy-2-cetyl-stearyl ether/cetyl alcohol

2.5 g

- Monoisopropanolamide of copra acid, available under the name EMPILAN CIS from MARCHON

1.5 g

- Polydiorganosiloxane with a thiol functional group (X2 8360), available from DOW CORNING, according to the formula:



2 g AI

- Preservative, perfume, q.s.p.  
pH adjusted to 6.5 with hydrochloric acid.

100 g

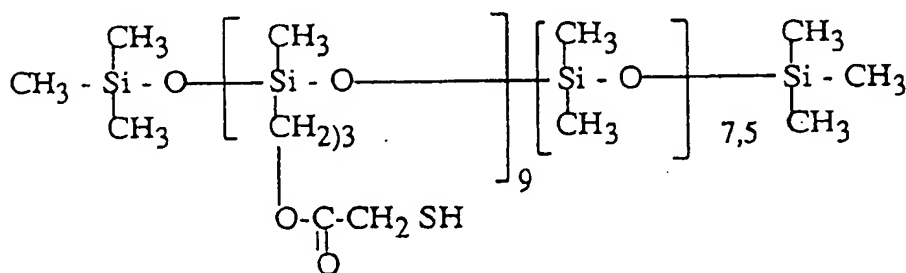
This composition is used as a shampoo for shampooing the hair.

### EXAMPLE 4

- Polyacrylamide dispersion available under the name SEPIGEL 305 from SEPPIC

1 g AI

- Polydiorganosiloxane with a thiol functional group according to the formula:



3 g

- Mixture of  $\alpha$ - $\omega$  dihydroxy-PDMS/cyclotetra- and cyclopentadimethylsiloxane

15 g

- Water, q.s.p.

100 g

- pH adjusted to 7 with sodium hydroxide.

This composition is used by application, not following by rinsing, for the treatment of dyed hair.



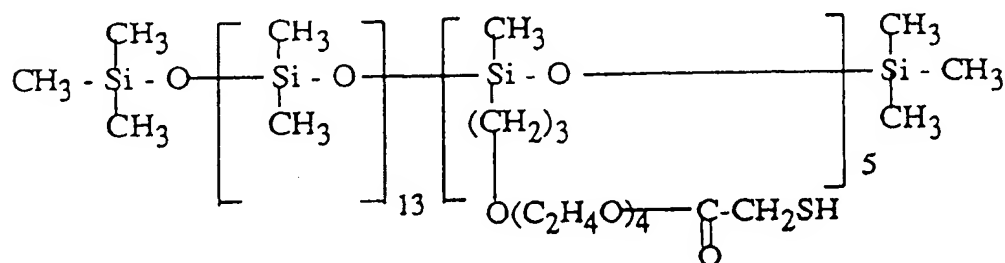
**EXAMPLE 5**

- Carboxyl polymer available under the name CARBOPOL 940 from GOODRICH —

2 g

- Polydiorganosiloxane with a thiol functional group according to the formula:

8 g



- Colorants, perfume

- Water, q.s.p.

100 g

pH adjusted to 6 with triethanolamine

This composition is applied to dyed hair, which is then dried and the hair is done without intermediate rinsing.

**EXAMPLE 6**

- Vinyl acetate/vinyl *p-tert.*-butyl benzoate/crotonic acid terpolymer (65:25:10)

8.65 g

- 2-Amino-2-methyl-1-propanol

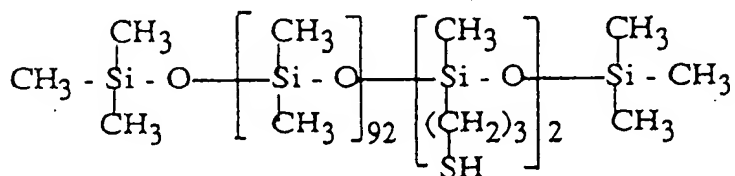
0.86 g

- Tripropylene glycol monoethyl ether available under the name DOWANOL TPM from DOW CHEMICAL

0.43 g

- Polydiorganosiloxane with a thiol functional group, available from DOW CORNING under the name X2 8360, according to the formula:

1.5 g



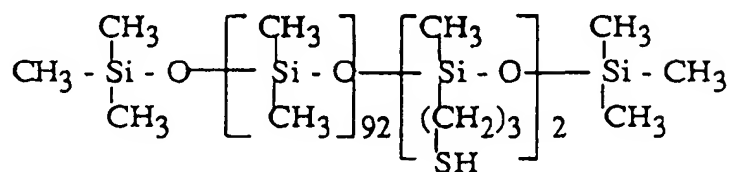
- Absolute ethyl alcohol, q.s.p.

100 g

This composition is used as a hair lacquer for fixing the hair.

**EXAMPLE 7**

- Polydiorganosiloxane with a thiol functional group



available under the name X2 8360 from DOW CORNING

- Cyclotetradimethylsiloxane

- Cyclopentadimethylsiloxane

- Isopar H, available from Exxon, q.s.p.

5 g

35 g

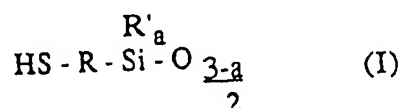
35 g

100 g

The compositions according to Examples 1 and 2, applied to dyed hair in the usual manner, protect the color of the hair from shampooing and light while conferring softness, shine and lightness.

**Claims**

1. Use of a polydiorganosiloxane with a thiol functional group containing in its molecule at least one unit according to the formula:

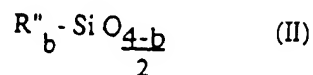


in which:

R denotes a divalent aliphatic radical containing 3 to 26 carbon atoms, which is possibly interrupted with an ester functional group and may contain ethylene oxide or propylene oxide or their mixtures as repeat units;

R' denotes a monovalent hydrocarbon radical containing 1 to 6 carbon atoms, an alkoxy radical containing 1 to 4 carbon atoms, or trimethylsilyloxy;

a denotes an integer equaling 0, 1 or 2, the other units corresponding to the formula:



in which:

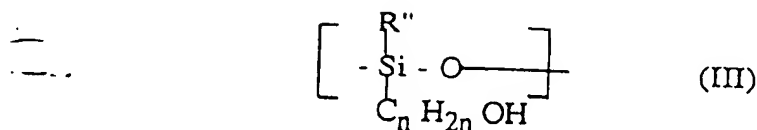
R'' denotes a C<sub>1</sub>-C<sub>18</sub> alkyl group, a (C<sub>1</sub>-C<sub>6</sub>) phenylalkyl group or a phenyl group;

b is an integer equaling 1, 2 or 3;

at least 50% of the groups R' and R'' denoting a methyl radical, as an agent for protecting the color of dyed keratin fibers.

2. Use in accordance with claim 1, in which the polyorganosiloxane also contains units according to the formula:

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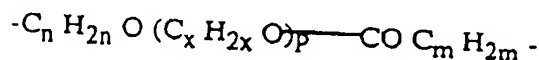


R'' having the meaning given in claim 1, and  $n$  being an integer equaling 1 to 18.

10

3. Use in accordance with claim 1 or 2, in which the polyorganosiloxane contains a unit according to formula (I), in which R denotes an alkylene group containing 3 to 8 carbon atoms, or a group according to the formula:

15

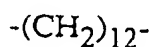
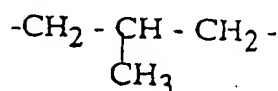
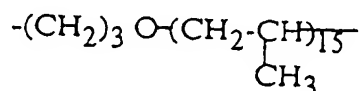
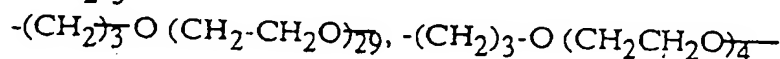
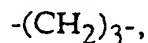


in which  $n$  denotes an integer ranging from 1 to 18,  $m$  denotes an integer ranging from 1 to 8,  $x = 2$  or 3, and if  $x = 3$ , the radical  $\text{C}_3\text{H}_6$  is branched[,]  $p$  equals 0 or denotes a number of up to 40.

20

4. Use in accordance with any of the claims 1 through 3, characterized in that the polydiorganosiloxane with a thiol functional group corresponding to the definition given in claim 1 is selected from among the compounds in which R denotes:

25



30

35

R' denoting  $\text{CH}_3$  or trimethylsilyloxy, R'' denoting  $\text{CH}_3$ ,  $\text{Cl}_2\text{H}_{25}$ , 2-phenylpropyl, the total number of the units (I) and (II) being less than or equal to 500.

40

5. Use in accordance with any of the claims 1 through 4, characterized in that polydiorganosiloxanes with a thiol functional group are used in which the amount of the thiol groups present on a weight basis is between 0.1% and 15% and preferably between 0.15% and 13%.

45

6. Use in accordance with any of the claims 1 through 5, characterized in that the polydiorganosiloxane with a thiol functional group is used by using a composition containing at least 0.1 wt. % of the said polydiorganosiloxane with a thiol functional group in a carrier suitable for being applied to dyed keratin fibers.

7. Composition intended for application to dyed keratin fibers and, in particular, to dyed human hair, for protecting the hair from degradation caused by external agents, characterized in that it contains, in a medium suitable for being applied to keratin fibers, at least 0.1% of a polydiorganosiloxane with a thiol functional group as defined in any of the claims 1 through 6.
8. Composition in accordance with claim 7, characterized in that the composition is in the form of an oily lotion, emulsion, aqueous or water-alcohol dispersion.
9. Composition in accordance with claim 7 or 8, characterized in that the oily lotions contain mineral, vegetable, animal or synthetic oils, besides the polydiorganosiloxane with a thiol functional group.
10. Composition in accordance with claim 9, characterized in that the oils are selected from among the silicone oils or the isoparaffins.
11. Composition in accordance with claim 10, characterized in that the silicone oils are oils with a linear or cyclic structure selected from among the polyalkylsiloxanes, the polyarylsiloxanes, the polyalkylarylsiloxanes, and the polyorganosiloxanes modified with organic functional groups different from the thiol group and their mixtures.
12. Composition in accordance with any of the claims 7 through 11, characterized in that the oily lotions also contain waxes, resins or silicone gums.
13. Composition in accordance with claim 7 or 8, characterized in that it is in the form of a non-ionic or cationic emulsion.
14. Composition in accordance with claim 13, characterized in that the fatty phase of the emulsions is formed either by the polydiorganosiloxane with a thiol functional group as defined in any of the claims 1 through 6 or a mixture of this polydiorganosiloxane with a thiol functional group with other oils or waxes.
15. Composition in accordance with claim 13, characterized in that it is in the form of a non-ionic emulsion containing a non-ionic emulsifying agent selected from among the polyethoxylated fatty alcohols, the polyethoxylated fatty acids, the optionally polyethoxylated sorbitan esters, the polyethoxylated or polyglycerolated alkyl phenols, the polyglycerolated fatty alcohols and alpha-diols.
16. Composition in accordance with claim 7 or 8, characterized in that the composition is in the form of a cationic emulsion containing a cationic emulsifying agent selected from among the quaternary ammonium halides.
17. Composition in accordance with claim 7 or 8, in the form of an aqueous dispersion, characterized in that it also contains water and a dispersing agent besides the polydiorganosiloxane with a thiol functional group as defined in any of the claims 1 through 6.
18. Composition in accordance with claim 17, characterized in that the dispersing agent is formed by a copolymer of ammonium acrylate with crosslinked acrylamide.

19. Composition in accordance with any of the claims 7 through 18, characterized in that it is in the form of a spray or is pressurized in an aerosol.
- 5 20. Composition in accordance with claims 7 or 8, characterized in that it is in the form of an alcohol-based lotion containing, in addition to the polydiorganosiloxane with a thiol functional group, a lower alcohol containing 2 to 4 carbon atoms and possibly other organic solvents.
- 10 21. Process for protecting the artificial color of dyed hair, characterized in that a composition containing, in a medium suitable for the hair, at least 0.1 % of a polydiorganosiloxane containing a thiol functional group as defined in any of the claims 1 through 6, is applied to the hair.